

Quantitative Determination of the Adiabatic Condition Using Force-Detected Nuclear Magnetic Resonance

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The adiabatic condition governing cyclic adiabatic inversion of proton spins in a micron-sized ammonium chloride crystal was studied using room temperature nuclear magnetic resonance force microscopy. A systematic degradation of signal-to-noise was observed as the adiabatic condition became violated. A theory of adiabatic following applicable to cyclic adiabatic inversion is reviewed and implemented to quantitatively determine an adiabaticity threshold $(\gamma H_1)^2/(\omega_{osc}\Omega) = 6.0$ from our experimental results.

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I. INTRODUCTION

The theory of magnetic resonance force microscopy (MRFM) was first presented by John Sidles in 1991¹. A recent experiment succeeded in the first MRFM-based detection of a single electron spin². The basic idea of MRFM is that if the magnetic moment, \mathbf{m} , of a sample is modulated in time in the presence of a magnetic field gradient, $\nabla \mathbf{B}$, then there will be an oscillatory force coupling the two given by $\mathbf{F}(t) = \mathbf{m}(t) \cdot \nabla \mathbf{B}$. In practice, as illustrated in Fig. 1 for MRFM using nuclear spins (NMRFM), the sample is mounted on a low spring constant mechanical oscillator, the field gradient is supplied by a permanent magnet, and the nuclear magnetization is manipulated using radio frequency (*rf*) magnetic fields; alternatively, one places a small magnet on the oscillator in order to scan arbitrary samples^{3,4,5,6}. The deflection of the oscillator due to the force $\mathbf{F}(t)$ is detected with a fiber optic interferometer. If the sample's magnetization varies in time with a frequency equal to the resonance frequency of the oscillator, then the deflection amplitude is

increased by the quality factor, Q , of the oscillator. The minimum detectable force of an NMRFM experiment is limited by the thermal noise of the mechanical oscillator, given by $F_{min} = \sqrt{4k_{osc}k_B T \Delta\nu/(\omega_{osc}Q)}$, where k_{osc} and ω_{osc} are the spring constant and resonance frequency of the mechanical oscillator, k_B is Boltzmann's constant, T is the temperature, and $\Delta\nu$ is the equivalent noise bandwidth of the measurement⁷.

The relaxation of spins during measurement is a detriment to signal strength, and is a subject of ongoing research^{8,9,10,11,12,13,14}. The regimes of spin manipulation can be classified by the relative magnitudes of the spin relaxation rate and the resonance frequency of the mechanical oscillator. Cyclic adiabatic inversion, interrupted cyclic adiabatic inversion, and cyclic saturation are applied when the relaxation rate is much less than, of the same order, or much greater than the resonance frequency of the mechanical oscillator, respectively. The focus of this study is on cyclic adiabatic inversion and the level of adiabaticity required to manipulate the maximum number of spins for a given set of experimental parameters when relaxation is negligible.

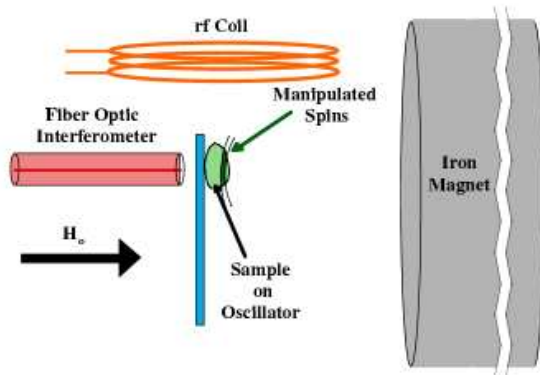


FIG. 1: (Color online) Experimental setup for the sample-on-oscillator configuration used in this study.

II. CYCLIC ADIABATIC INVERSION

Cyclic adiabatic inversion is superficially identical to the conventional adiabatic rapid passage technique¹⁵. However, instead of one sweeping pass, cyclic adiabatic inversion repeats many adiabatic rapid passages so as to make the \hat{z} component of the sample magnetization, M_z , periodic. In samples with relaxation rates much less than the oscillator resonance frequency, spins will lock to the effective field throughout a truly adiabatic cyclic inversion. The slowly varying effective magnetic field essentially looks static to such spins, and they readily precess around and follow it as it changes in time.

The description of cyclic adiabatic inversion is mathematically straightforward. The effective field in the rotating frame (designated by primed unit vectors), \mathbf{H}_{eff} ,

can be generically written as $(H_o - \omega_{rf}/\gamma)\hat{z} + H_1\hat{x}'$, where H_o is the total polarizing field, γ is the gyromagnetic ratio of the sample spins, and ω_{rf} and H_1 are the angular frequency and magnitude of the rotating rf field, respectively. Cyclic adiabatic inversion is achieved by frequency modulation (fm) of the rf field. The carrier frequency is the Larmor frequency of the spins $\omega_o = H_o/\gamma$, the modulation frequency is the resonance frequency of the mechanical oscillator ω_{osc} , and the fm amplitude is Ω . The \hat{z} component of the effective field can thus be written $\mathbf{H}_{eff} \cdot \hat{z} = H_o - (\omega_o + \Omega \sin(\omega_{osc}t))/\gamma$. The \hat{z} component of the magnetization of the sample has the same time dependence since the spins are locked to the oscillating effective field. The oscillating sample magnetization in the presence of a field gradient thus results in a time varying force that resonantly excites the mechanical oscillator.

In its simplest form, the adiabatic condition governing cyclic adiabatic inversion says that the effective Larmor frequency of the spins must be much greater than the rate of change of the effective field. Translating this into a specific mathematical statement depends on the particular inversion scheme, but in general can be written as $(\gamma H_{eff})_{min} \gg (d\phi/dt)_{max}$, where $(\gamma H_{eff})_{min}$ is the minimum Larmor frequency of the spins, $(d\phi/dt)_{max}$ is the maximum angular frequency of the effective field in the rotating frame, and ϕ is defined by $\tan \phi = (\mathbf{H}_{eff} \cdot \hat{z})/(\mathbf{H}_{eff} \cdot \hat{x}')$. In our case, we have $\mathbf{H}_{eff} = (H_1, 0, (\Omega/\gamma) \sin(\omega_{osc}t))$. Taking $(\gamma H_{eff})_{min} = \gamma H_1$, and evaluating the time derivative of ϕ , leads to the statement of the adiabatic condition specific to sinusoidal cyclic adiabatic inversion:

$$\frac{(\gamma H_1)^2}{\omega_{osc}\Omega} \gg 1. \quad (1)$$

Written in this manner, the adiabatic condition compares experimental parameters to unity, with a large number implying the adiabatic condition is well met.

Equation 1 implies the importance of the three major experimental parameters ω_{osc} , H_1 , and Ω . Of these, Ω is the most experimentally flexible; ω_{osc} is fixed by the structure of the oscillator, and in this experiment a spurious signal artifact associated with the rf limits H_1 to about 7 G. In contrast, Ω can be changed over two decades.

There is a limit to the magnitude of the magnetization we can manipulate for a given set of parameters, even if we assume the adiabatic condition is well met and do not consider relaxation. The time varying \hat{z} component of the magnetization can be written as

$$M_z(t) = M_o \frac{\frac{\Omega}{\gamma} \sin \omega_{osc}t}{\sqrt{(\frac{\Omega}{\gamma} \sin \omega_{osc}t)^2 + H_1^2}},$$

where M_o is the equilibrium sample magnetization following Curie's Law. The maximum manipulable magnetization is thus

$$\left(\frac{M_z}{M_o}\right)_{max} = \frac{1}{\sqrt{1 + (\frac{\gamma H_1}{\Omega})^2}}. \quad (2)$$

We see that the maximum magnetic moment per unit volume contributing to a force signal through cyclic adiabatic inversion will always be less than the equilibrium magnetization. The participating magnetization should increase with increasing Ω , for all other parameters constant. However, comparison with the adiabatic condition shows that increasing Ω decreases the level of adiabaticity. There is clearly a competition between these two that determines the signal strength. If adiabaticity is achieved, the signal should be consistent with Eq. 2. Violations of the adiabatic condition would result in deviations from this behavior.

III. EXPERIMENTAL DETAILS

This proton NMRFM experiment was performed in a uniform 8.073 T external magnetic field in the sample-on-oscillator configuration (Fig. 1). The experiment was performed at room temperature in a vacuum of 15 mTorr. An ammonium chloride (NH_4Cl) crystal was mounted onto the head of a double torsional oscillator using a thin glass fiber and N-grease. The sample was a flat cylinder roughly 10 μm thick and 25 μm in diameter. This salt was chosen for its abundance of protons ($6.9 \times 10^{22} \text{ }^1\text{H}/\text{cm}^3$) and its long room temperature spin-lattice relaxation time ($T_1 \sim 3 \text{ s}$). Note that in the short correlation time regime $T_1 \sim T_{1\rho}$.

The mechanical oscillator was a single-crystal silicon double torsional oscillator^{16,17,18}. The first cantilever mode of the oscillator was used, which had a resonance frequency of 7 kHz, a pressure-limited quality factor of 900, and an estimated spring constant of 10^{-2} N/m . The minimum detectable force at room temperature using a 2.5 Hz measurement bandwidth was thus $3.3 \times 10^{-15} \text{ N}$.

The permanent magnet that provided the field gradient was an iron cylinder that was molded in a zirconium gettered, argon atmosphere arc furnace. The cylinder was 44.0 mm long, and had a radius of 0.76 mm. Modelling was used to estimate the axial field, \mathbf{B}_z , and field gradient, $\nabla_z \mathbf{B}$. A reasonable estimate of the resonance slice thickness (i.e., resolution) is¹⁹

$$\Delta z = \frac{2\Omega}{\gamma \nabla_z \mathbf{B}}. \quad (3)$$

For the purpose of this experiment, however, spacial resolution of the sample was not a concern. Accordingly, we chose to operate at a comfortable magnet-to-sample distance of 1 mm, where $\nabla_z \mathbf{B}$ was 310 T/m. This field gradient and our fm amplitude range of $\Omega/2\pi \in [5, 40 \text{ kHz}]$ corresponded to resonance slice thicknesses $\Delta z \in [0.8, 6.0 \text{ } \mu\text{m}]$. The field \mathbf{B}_z at 1 mm was 0.191 T, resulting in a total polarizing field of 8.264 T, and a proton Larmor frequency of 351.8 MHz. Using Curie's Law to calculate the equilibrium magnetization of the sample, and taking the volume of spins contributing to the signal to be $a\Delta z$, where a is the cross sectional area of the sample, the theoretical force for $\Omega/2\pi = 40 \text{ kHz}$ was $5.7 \times 10^{-14} \text{ N}$, leading to a theoretical

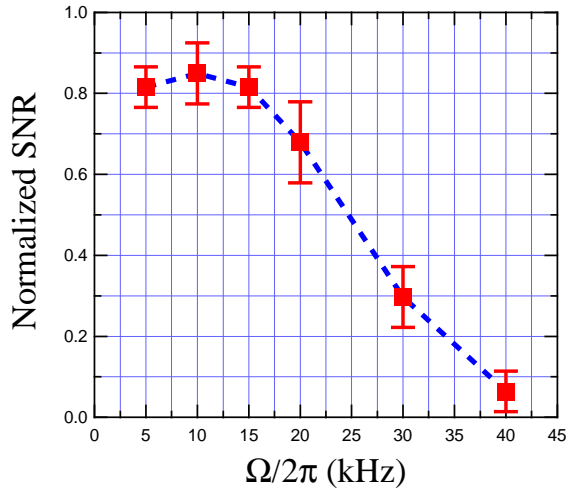


FIG. 2: (Color online) Normalized SNR as a function of the frequency modulation amplitude. The observed decrease occurs as the adiabatic condition is violated.

signal-to-noise ratio (SNR) of 17; the theoretical SNR for $\Omega/2\pi = 5$ kHz was 2.

For each value of $\Omega/2\pi$, with a constant H_1 of 7 G, the iron magnet was moved in 3 μm steps so that the resonance slice scanned through the sample. We performed and averaged 5-8 cyclic adiabatic inversion sequences at each position. The signal from each position was determined using the *rms* value of a 100 ms long section of the time series, starting ~ 30 ms after the oscillator reached its driven equilibrium amplitude. Due to the long relaxation time of proton spins in NH_4Cl , the temporal response of the signal showed no degradation over the investigated time scale. The baseline was subtracted from the signal at each position to determine the NMR-induced oscillator amplitude. The NMR origin of the signal was verified by observing the signal shift 100 μm when the *rf* carrier frequency was increased by 1 MHz.

Figure 2 presents normalized SNR (nSNR) data as a function of the frequency modulation amplitude taken with the resonance slice in the center of the sample. We define nSNR as the experimental SNR normalized by the theoretical SNR for each Ω . Using nSNR implicitly accounts for signal changes due to the Ω -dependence of both the maximum manipulable magnetization (Eq. 2) and the resonance slice thickness (Eq. 3). Thus, when the measured signal is in accord with the expected signal, nSNR should be independent of the experimental parameters that comprise the adiabaticity factor. The data of Fig. 2 show such behavior for $\Omega/2\pi$ of 15 kHz and below. In this region, the maximum number of spins per unit volume were engaged in cyclic adiabatic inversion. In contrast, the adiabatic condition became violated as $\Omega/2\pi$ was increased above 15 kHz. Here, the effective field moved too rapidly for the proton spins to follow, resulting in a degradation of nSNR. Similar behavior can be inferred from ^{19}F data in CaF_2 from a

previous study²⁰. A systematic error in calculating the theoretical signal or theoretical sensitivity is most likely responsible for the nSNR not reaching unity; this error has no Ω dependence.

IV. THEORETICAL FORMALISM

Here we describe a theory set forth by Sawicki and Eberly in the context of quantum optics²¹, but now discussed in the framework of nuclear magnetism and cyclic adiabatic inversion. An essential assumption for the reasonable application of this theory is that the relaxation of locked spins is negligible. This requirement was met in our case as the relevant relaxation times of the proton spins were three orders of magnitude larger than the time for a single inversion π/ω_{osc} , and more than one order larger than the cyclic adiabatic inversion time series. We propose that the following theory may be applied to multiple inversions without loss of generality when relaxation phenomena may be ignored.

Taking the magnetization in the rotating frame at equilibrium to be $\mathbf{M} = (0, 0, 1)$, the time evolution of the Bloch-vector \mathbf{M} is given by

$$\frac{d\mathbf{M}}{dt} = \gamma \mathbf{H}_{eff} \times \mathbf{M}, \quad (4)$$

where \mathbf{M} rotates about the effective field. As a first approximation to cyclic adiabatic inversion, assume the effective field in the rotating frame is uniformly rotating with constant angular velocity A in the $\hat{x}'\text{-}\hat{z}$ plane about the vector $\mathbf{A} = A\hat{y}'$. The time evolution of $\gamma \mathbf{H}_{eff}$ is then

$$\frac{d(\gamma \mathbf{H}_{eff})}{dt} = \mathbf{A} \times \gamma \mathbf{H}_{eff}. \quad (5)$$

The effective field then becomes $\gamma \mathbf{H}_{eff} = (\pm \gamma H_{eff} \sin At, 0, \pm \gamma H_{eff} \cos At)$. The spin-locking solution that satisfies both Eq. 4 and Eq. 5 is $\mathbf{M} = \pm (\gamma \mathbf{H}_{eff}(t) - \mathbf{A}) \xi$. The constant ξ has units of time and is under the constraint $\mathbf{M} \cdot \mathbf{M} = 1$, which is to say $(\gamma H_{eff}^2 + A^2)\xi^2 = 1$, where A is the angular velocity of $\gamma \mathbf{H}_{eff}$ about \mathbf{A} . The exact solution for the Bloch vector in the rotating frame is

$$\begin{aligned} M_{x'} &= A\xi \sin(t/\xi) \cos(At) \\ &\quad - (1 + A^2\xi^2(\cos(t/\xi) - 1) \sin(At)), \\ M_{y'} &= \gamma H_{eff} A\xi^2(\cos(t/\xi) - 1), \\ M_z &= -A\xi \sin(t/\xi) \sin(At) \\ &\quad - (1 + A^2\xi^2(\cos(t/\xi) - 1)) \cos(At). \end{aligned}$$

The object of interest for adiabatic inversion is the probability of spins following $\gamma \mathbf{H}_{eff}$ through a rotation of π radians, P_π . Assuming no spin relaxation, a trivial extension of the work of Sawicki and Eberly finds P_π for the inversion time $t = \pi/A$ to be

$$P_\pi = 1 - \frac{\Lambda^2}{1 + \Lambda^2} \sin^2 \left(\frac{\pi}{2} \frac{\sqrt{1 + \Lambda^2}}{\Lambda} \right), \quad (6)$$

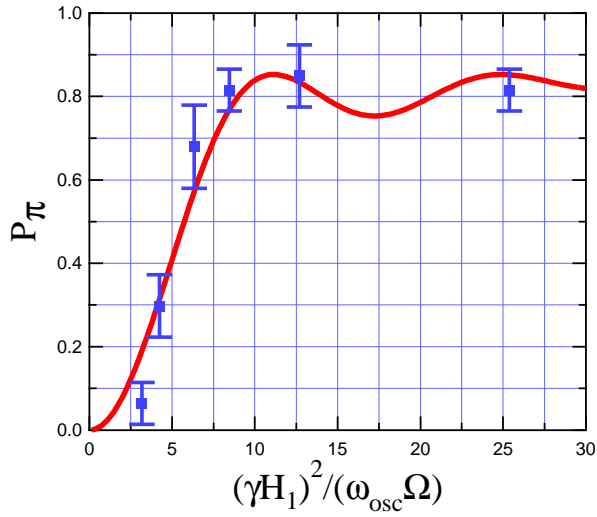


FIG. 3: (Color online) Fit of experimental data using the adiabatic following theory of Eq. 6.

where we have introduced a diabaticity parameter $\Lambda \equiv A/\gamma H_{eff}$. This parameter compares the angular velocity of the rotating effective field to the angular velocity of the spins about the effective field. Thus, $P_\pi \rightarrow 1$ in the adiabatic limit of $\gamma H_{eff} \gg A$, and $P_\pi \rightarrow 0$ in the diabatic limit of $A \gg \gamma H_{eff}$.

V. DISCUSSION

To compare experimental cyclic adiabatic inversion data with Eq. 6, we make the identification $1/\Lambda = (\gamma H_1)^2/(\omega_{osc}\Omega)$. Furthermore, we introduce two fitting parameters, s and n , and make the transformation $P_\pi(\Lambda) \rightarrow sP_\pi(n\Lambda)$. Fig. 3 shows a least squares fit of our experimental data to this function, where the best fit parameters were $s = 0.85$ and $n = 6.4$. We define the adiabatic threshold as the value of $(\gamma H_1)^2/(\omega_{osc}\Omega)$ for which the best fit comes within $1/e$ of its maximum. We thus determine an adiabatic threshold of 6.0 for protons in NH_4Cl .

The non-uniform rotation of the experimental effective field makes the adiabatic condition of Eq. 1 a conservative statement as it considers the *minimum* Larmor frequency and the *maximum* angular velocity of the effective field. Experimentally, both of these, and thus the adiabatic factor, are time dependent. The adiabaticity threshold

of 6.0 corresponds to the worst case scenario, which is experienced on resonance ($\mathbf{H}_{eff} = H_1 \hat{x}'$). Further theoretical development is necessary to define an adiabaticity threshold for non-uniform rotation.

The discrepancy between the specific way in which spins are inverted in this theory and our experiment is a minor one. The theory considers an effective field uniformly rotating in the \hat{x}' - \hat{z} plane. Experimentally, only the \hat{z} -component of \mathbf{H}_{eff} is time-dependent. In fact, the theoretical effective field projected onto the line $x' = H_1$ is exactly the experimental effective field. If there is true adiabatic following, the spins should follow both descriptions of the effective field equally well. Further, the experiment is only sensitive to the \hat{z} -component of the magnetization, which is identical in the theory and the experiment. It is thus quite reasonable that this theoretical treatment applies to adiabatic inversion. However, it is curious, and perhaps specific to this type of spin system, that a theory concerning a single π inversion applies to cyclic inversions. Additional research is needed to further elucidate this phenomenon, and to comment on the general applicability of the theory.

VI. CONCLUSION

We have investigated the level of adiabaticity necessary to perform room temperature cyclic adiabatic inversion of proton spins in an ammonium chloride crystal using nuclear magnetic resonance force microscopy. We observed a systematic degradation of signal-to-noise as the adiabaticity factor decreased below this level. A theory of adiabatic following was discussed to describe cyclic adiabatic inversion in terms of experimentally relevant parameters, and was utilized to quantitatively determine an adiabaticity threshold $(\gamma H_1)^2/(\omega_{osc}\Omega) = 6.0$ from our experimental results.

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